

# Direct Measurement of Spatial Distortions of Charge Density Waves in $K_{0.3}MoO_3$

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Using X-ray scattering and the technique of multiple diffractions, we revisit the dynamical transition of charge density waves (CDWs) in  $K_{0.3}MoO_3$  under applied voltages. In addition to the usual transport and half width (of Bragg peaks) measurements, we also measure the triplet phase by three-wave diffraction, which provides, for the first time, the *direct* evidence for the spatial distortions of CDWs. This novel and sensitive technique developed here can be applied to general periodic media, including stripes in high temperature superconductors, and provide a new perspective into interesting phenomena in these materials.

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The homogeneous phases in low dimensional materials, such as  $K_{0.3}MoO_3$ ,  $NbSe_3$  and TMTSF molecules, undergo a phase transition to charge density waves (CDWs) at low temperatures. The instability toward spontaneous formation of charge-density modulations is driven by electron-phonon interactions, or sometimes electron-electron ones [1]. Among many other interesting aspects of CDW, transport property in the presence of finite driving electric field has attracted lots of attentions from both experimental and theoretical sides. It is generally believed that the current is suppressed at small biased voltage, where the CDW is pinned by impurity potential. Above some threshold voltage, the sliding motion along the applied electric field starts and the current increases significantly. It has been known that this dynamic behaviour involves the phase slippage of the density waves. In fact, similar phenomena occurs in many other systems, such as moving vortex lattice [2], Wigner crystal [3], charge/spin stripes in CMR, high- $T_C$  superconductors [2, 4] and  $La_{2-x}Sr_xNiO_4$  [5, 6], colloids [7], magnetic bubbles [8] and so on.

We revisit this well-studied transition in this Letter, attempting to measure the distortions of CDW in pinned and sliding phases directly. In previous studies, the sliding transition is spotted by sudden jump in  $I - V$  characteristics at low temperatures [9] and/or the half-width change of the Bragg peaks [10]. Theoretical investigations [11, 12] predicted that the pinning forces become irrelevant when the system enters the sliding phase. This indeed provides a natural explanation for the dynamical narrowing of the half width above the threshold voltage. However, to understand how the CDW adjusts to the pinning forces at different driving voltages, a direct measurement for the spatial distortions of CDW is desirable. In this Letter, in addition to the usual transport and FWHM (full width at half maximum) measurement of the CDW satellite reflections, we first establish the

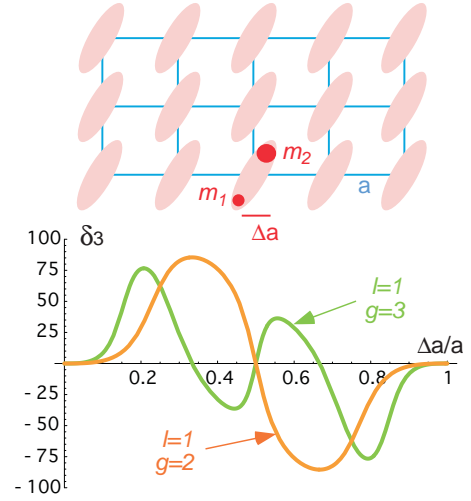


FIG. 1: (Color online) (a) (up) Two-dimensional square lattice with distortion  $\Delta a$ , (b) (bottom) Triplet phase  $\delta_3$  versus the distortion  $\Delta a/a$ . Two specific choices  $l = 1, g = 2$  and  $l = 1, g = 3$  are presented here.

connection between the lattice distortions and the triplet phase in X-ray scattering and thus demonstrate how the spatial distortions of CDW can be measured directly. While the sliding transition is already well studied, the technique we developed here can be applied to general periodic media driven by external sources and provides a new perspective into many interesting strongly correlated systems.

Since the triplet phase  $\delta_3$  plays an essential role in our study, it is helpful to illustrate its physical meaning and connections to lattice distortions first. The triplet phase  $\delta_3$  is defined as the phase of the structure factor triplet  $F_{G_2}F_{G_3}/F_{G_1}$ , where  $G_i$  are reciprocal lattice vectors, satisfying  $G_1 = G_2 + G_3$ . [13, 14, 15]. Since they form a closed triangle in the reciprocal vector space, it

is straightforward to show that the triplet phase  $\delta_3$  is invariant under arbitrary choices of unit cells [16]. This invariance provides a hint for its connection to some physical quantity, which turns out to be the internal distortion of the unit cell. Experimentally, this triplet phase can be determined by measuring the diffracted intensity profiles of a three-wave ( $O, G_1, G_2$ ) diffraction involving the primary  $G_1$ , the secondary  $G_2$ , and the coupling  $G_3 = G_1 - G_2$  reflections, where  $O$  stands for the direct reflection of the incident beam [13]. Let's consider a two-dimensional square lattice with two ions in one unit cell, as shown in Fig. 1. Without distortion  $\delta a = 0$ , the lattice has inversion symmetry which ensures all structure factors are real (under appropriate choice of the unit cell) and thus gives  $\delta_3 = 0$ . Under the driven voltage, the CDW is distorted and twists the underlying lattice as well. For simplicity, let's assume that it can be described by a lattice twist  $\delta a$  along direction of CDW ( $x$ -axis here). Furthermore, let's choose the reciprocal lattice vectors to be along the direction of CDW, i.e.  $G_1 = (2g\pi/a, 0)$ ,  $G_2 = (2l\pi/a, 0)$  and  $G_3 = G_1 - G_2$ . The resultant triplet phase can be computed straightforwardly,

$$\tan \delta_3 = \frac{\Delta \sum_i \sin(G_i \delta a + \varphi_i)}{r + \sum_i \cos(G_i \delta a)}, \quad (1)$$

where  $\varphi_1 = \pi$  and  $\varphi_{2,3} = 0$ . The other parameters are  $\Delta = (m_1 - m_2)/(m_1 + m_2)$  and  $r = (m_1^3 + m_2^3)/2m_1m_2(m_1 + m_2)$ . Two particular choices of  $l$  and  $g$  are given in Fig. 1 to demonstrate the connection between the triplet phase  $\delta_3$  and the lattice distortion  $\delta a$ .

In realistic setup, the lattice distortion is rather small  $\delta a/a \ll 1$  at all applied voltages, thus the expression of the triplet phase simplifies,  $\delta_3 \sim (\delta a/a)^3$ . Note that the cubic dependence is *generic* due to the inversion symmetry of the undistorted lattice and the close triangle formed by  $G_i$ . While this result is derived from the simple model, it captures the generic dependence of the triplet phase even for the more complicated crystal  $\text{K}_{0.3}\text{MoO}_3$  we studied here. Therefore, the triplet phase provides a direct measurement of the spatial distortions of CDWs at different driving voltages.

Now we turn to the experimental details and the observed results of transport and X-ray measurements. A single crystal  $\text{K}_{0.3}\text{MoO}_3$  of good quality was prepared for the transport measurement and X-ray scattering. The crystal structure belongs to the monoclinic with the space group  $C2/m$ . The lattice parameters of  $\text{K}_{0.3}\text{MoO}_3$  are  $a = 18.162 \text{ \AA}$ ,  $b = 7.554 \text{ \AA}$ ,  $c = 9.816 \text{ \AA}$ , and  $\beta = 117.393^\circ$  [17]. The sample, with transition temperature around 180 K, was characterized with a mosaic width of  $0.005^\circ$  and pre-aligned using an X-ray rotating anode source so that the scattering plane coincided with  $a^* \times c^*$  plane. The in-situ measurements were carried out on the Taiwan beamline BL12B2 of SPring-8 synchrotron facility. The incident x-ray wavelength was selected to be  $1 \text{ \AA}$ .

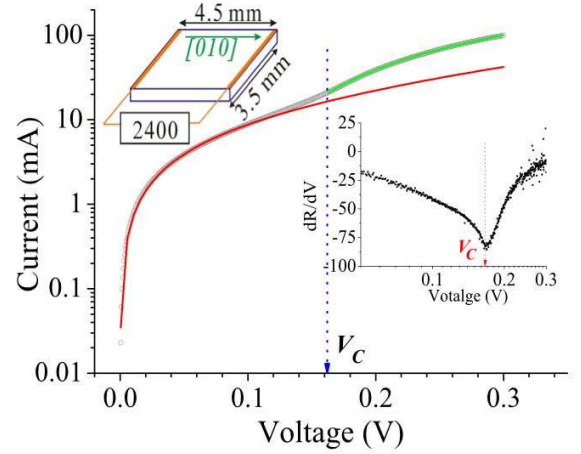


FIG. 2: (Color online)  $I - V$  characteristic of  $\text{K}_{0.3}\text{MoO}_3$  in a two-probe transport setup at  $T = 70 \text{ K}$ . The red line is the fit to the predicted thermal creeps when the CDW is pinned. The left inset shows the dimension of the sample and the experimental setup. The right inset for  $(dR/dV)$  shows a transition point at  $V_c = 0.165 \text{ V}$ .

Two gold stripes spaced about 3 mm were evaporated onto the sample surface as shown in the inset of Fig. 2. The sample was then glued on the cold head of a cryostat mounted on a 6-circle diffractometer. To drive current through the sample, the voltage was applied along  $b^*$  axis ( $[010]$  direction). A Keithley 2400 source meter was used to generate the driving voltage, and the  $I - V$  curve was measured by the two-probe setup. An upper limit of the current was set to 300 mA in order to protect the sample and meter.

Fig. 2 shows the non-linear conductivity of the sample at  $T = 70 \text{ K}$ , indicating the dynamical transition from the pinned CDWs to sliding motions. While the nonlinearity is not as robust as at low temperatures, the current below the critical voltage  $V_c \approx 0.165 \text{ V}$  can be fitted remarkably well with the prediction from thermal creep [9, 18, 19, 20, 21],

$$I(V) = G_0(V - V_0) \exp\left(\alpha \frac{V}{T}\right). \quad (2)$$

The parameters  $G_0$ ,  $V_0$  and  $\alpha$  are constants at all applied voltages. To make the critical transition more transparent, one can plot  $dR/dV$  (as shown in the inset of Fig. 2), which show clear singularity near the critical voltage  $V_c$ . The nice fit with the thermal creep behavior indicates that our two-probe measurement does not suffer poor contacts or serious current inhomogeneity in the sample. One may notice that there is no switching phenomena in our measured  $I - V$  curve due to thermal fluctuations at  $T = 70 \text{ K}$  [22, 23].

In addition to the transport measurement, the evolution of CDW satellite reflections as a function of applied fields was also probed using X-ray scattering. The

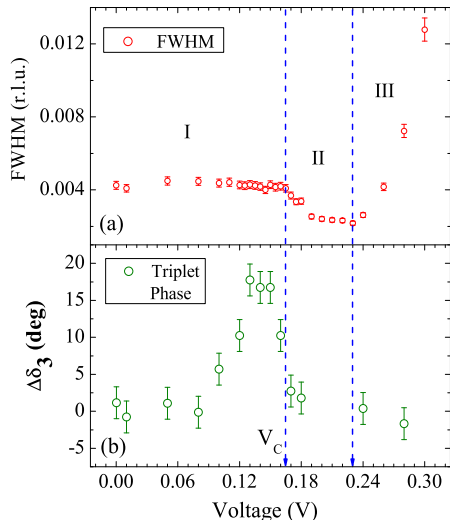


FIG. 3: (Color online) (a) Evolution of the half width of the Bragg peak versus the applied voltage. According to the changes of the half width, one can classify CDW into three phases: (I) the creeping CDW state, (II) the moving solid, and (III) the moving liquid. (b) The triplet phase change  $\Delta\delta_3$  at different voltages. Note that, in the sliding phase,  $\Delta\delta_3 = 0$  is a direct evidence that the pinning forces become irrelevant.

width of the CDW peak and triplet phase at different driving voltages are summarized in Fig. 3. In this Letter, we focus on the particular satellite reflection, located at  $G_1 = (13 \ q \ -6.5)$  with  $q \approx 0.748$ . Scans were performed along the longitudinal direction of  $[2 \ 0 \ -1]$  and the data were convoluted with resolution function obtained from nearby Bragg peak  $(12 \ 0 \ -6)$ . The FWHM of the primary reflection  $G_1$  in Fig. 3(a) remains more or less unchanged below the critical voltage  $V_c \approx 0.165$  V, determined from the transport measurement. Above the critical voltage, where the CDW enters the sliding phase, the FWHM decreases[24, 25] as predicted by previous theoretical investigations[24]. This interesting dynamical narrowing of half width is a strong indication that the pinning forces due to random potentials become irrelevant (or less efficient) when the CDW starts to slide[10, 21, 26]. In fact, similar motion-induced ordering behavior by external driving force has been reported in  $\text{NbSe}_3$  as well [10]. When the voltage goes beyond 0.22 V, other effects from non-equilibrium dynamics and amplitude fluctuations become important and the Bragg peaks disappear. This is clearly evidenced by the sharp increase of FWHM in Fig 3(a) and diminishing amplitude of the corresponding Bragg peak (not shown here).

Now we come to the central quantity we studied in this Letter – the triplet phase  $\delta_3$  of the 3-wave multiple diffraction at different biased voltages. To set up a 3-

wave ( $O, G_1, G_2$ ) multiple diffraction experiment, where  $O$  stands for the direct incident reflection, the crystal is first aligned for a primary reflection  $G_1$ . It is then rotated around the reciprocal lattice vector  $G_1$  with an azimuthal angle  $\psi$  to bring in the secondary reflection  $G_2$  which also satisfies Bragg's law. Namely, both  $G_1$  and  $G_2$  reflections take place simultaneously. The interaction of the multiply diffracted waves modifies the intensity of the primary reflection. Intensity variation showing asymmetric distribution versus  $\psi$ , giving the information about the triplet phase  $\delta_3$  of the three-wave structure factor  $F_{G_2}F_{G_3}/F_{G_1}$ [13, 14, 15]. Previously [27], we showed how the triplet phase  $\delta_3$  can be probed using multiple diffraction. Here we further demonstrate that measuring the change of the triplet phase  $\Delta\delta_3$  allows us to make direct observation of the internal deformations of the CDWs/lattice at different driving voltages.

The origin of azimuthal angle ( $\psi=0$ ) was determined to be the direction where  $[1 \ 0 \ 0]$  lay on the scattering plane. This can be verified by finding a mirror position in the multiple diffraction pattern of the primary reflection  $(6 \ 0 \ -3)$ . Through the azimuthal scan around the primary reflection  $G_1 = (13 \ q \ -6.5)$  at  $T = 70$  K, we obtained three-wave diffraction pattern containing lots of multiple diffraction peaks[28]. In this Letter, we concentrated only on the particular three-wave diffraction,  $G_1 = (13 \ q \ -6.5)$  and  $G_2 = (4 \ -8 \ 4)$  at  $\psi=108.53^\circ$ . Note that the coupling reflection is  $G_3 = G_1 - G_2 = (9 \ q + 8 \ -10.5)$ . The profile asymmetry of the diffraction intensity of  $G_1$  versus  $\psi$  at  $V = 0$  is typical because the triplet phase  $\delta_3 = 0$  due to the centrosymmetry of the undistorted lattice. Upon application of driving voltage, the change of the triplet phase  $\Delta\delta_3$  is analyzed based on the dynamical theory for multiple diffractions[13, 14, 15]. In Fig.4, the profiles with typical asymmetry ( $\Delta\delta_3 = 0$ ) and the distorted one ( $\Delta\delta_3 = 18^\circ$ ) are displayed. Note that the change in the peak profile for  $\Delta\delta_3 = 18^\circ$  indicates that the original centrosymmetry is broken due to lattice deformation caused by ion displacements under the influence of external forces. The measured  $\Delta\delta_3$  in Fig. 3(a) is very similar to the simplified calculation of triplet phase in Fig. 1 when the deformation is small  $\Delta a/a \ll 1$ . (Note that, in the present case,  $\Delta\delta_3 = \delta_3$  because the original value of  $\delta_3$  is zero for the undistorted lattice.) The Darwin width of a Bragg reflection was also monitored in order to make sure the crystal was not destroyed by the applied voltage. As shown in Fig. 3(b), the change of the triplet phase  $\Delta\delta_3$  hits its maximum at  $V = 0.12 \sim 0.14$  V. This clearly shows that the internal distortions of CDWs reach saturation just before the sliding motion. Loosely speaking (ignoring spatial inhomogeneity), at low bias voltages, the free energy is minimized by the small cost of elastic energy due to CDW distortions. After threshold voltage, it is energetically favorable to slide (costing kinetic energy) rather than holding up the large elastic energy. The estimated  $\Delta\delta_3$  from curve fitting at

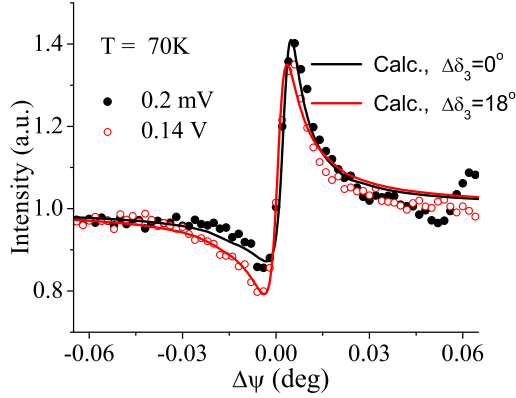


FIG. 4: (Color online) Triplet phase change  $\Delta\delta_3$  extrapolated from curve fitting of the 3-wave diffraction profiles for  $V = 0.2$  mV and 0.14 V: Since the primary ( $13\ q\ -6.5$ ) and the coupling reflection ( $9\ q\ +8\ 10.5$ ) are the fractional reflections, their structure factor amplitudes are much smaller than that of the secondary ( $4\ -8\ 4$ ) reflection. Also the amplitudes of ( $13\ q\ -6.5$ ) are nearly the same for  $V < 0.18$  V. Under this condition, the modification of profile asymmetry is dominated by the phase, rather than the amplitude of the structure-factor triplet. The analysis is based on the dynamic theory for multiple diffraction, giving  $\Delta\delta_3 = 0^\circ$  and  $18^\circ$  at  $V = 0.2$  mV and 0.14 V, respectively.

0.1, 0.12, 0.13, 0.14, 0.15, and 0.16 V are about  $6^\circ$ ,  $10^\circ$ ,  $18^\circ$ ,  $17^\circ$ ,  $17^\circ$ , and  $10^\circ$  respectively, and then back to  $0^\circ$  for  $V > V_c$ . As far as we know, this is the first *direct* observation of the spatial distortions of CDWs from the pinned to sliding states.[29, 30]

In summary, we demonstrate the simultaneous measurements of transport, half-width of the Bragg peak and the triplet phase of CDWs in  $\text{K}_0.3\text{MoO}_3$  at different driving voltages. The combination of different measurements provides evidence for the origin of the nonlinearity and dynamical phase transition in periodic media. In particular, the phase measurement using three-beam diffraction is demonstrated for the first time as a novel and sensitive method to probe dynamical phenomena in nonlinear systems. While it is already exciting to observe how the internal deformations respond through the dynamical transition of CDW, it also opens up many interesting issues requiring further studies. For instance, the powerful technique developed here can be used to study the crossovers/transitions between different types of dynamical phases and a global phase diagram at different temperatures and voltages can be mapped out without ambiguity. This technique can also be applied to general

periodic media, such as stripes/CDWs in high- $T_c$  related perovskites, and possibly deepen our understanding of dynamical motions in these materials.

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